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ABSTRACT

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This report covers the second quarter's work on a program to develop an electrolytic method for the preparation of high dielectric thin films. Results are reported for the anodization of niobium substrates in baths containing lead, cadmium and ethyl acid phosphate, titanium substrates in baths containing lead and barium, zirconium substrates in baths containing lead, and all three substrates in a number of other baths.

Titanium strips anodized in baths containing soluble lead species yielded films exhibiting higher capacity - voltage products than might be expected for single oxide component films. Niobium strips anodized at low forming potentials in basic plumbite baths produced thick films consisting of a conducting layer over a capacitive layer. These films exhibited breakdown potentials higher than their forming potentials.

Anodized niobium films contacted with potassium hydroxide and anodized titanium films contacted with barium hydroxide gave reactions indicating the possible formation of the corresponding niobate or titanate. Firing condition criteria in air and vacuum were obtained by firing titanium strips containing electrophoretic barium titanate deposits and zirconium strips containing anodized films. Adherent films were produced by anodizing at high, spark-producing current conditions. The possible utility of the spark method is indicated.

Author

Section I

INTRODUCTION

The objective of this investigation is the preparation of high dielectric thin films by electrolytic techniques. The background, experimental approach, and promising film constituents have been discussed in previous documents. (Refs. 1, 2).

The experimental work for this quarter has been concentrated on the investigation of baths containing soluble metal additives wherein the desired double metal oxide might be formed directly during the anodizing process - thus eliminating the difficult problem of reacting and sintering mixtures of oxides. Both component metals and substrate metals to be anodized were selected on the basis of combinations whose oxides give high dielectrics when prepared by ceramic techniques. Examples of such combinations are Ti substrates in Ba and Pb-containing baths and Nb substrates in K and Cd-containing baths, based on the high dielectric ceramics BaTiO_3 , PbTiO_3 , KNbO_3 and Cd_2NbO_7 . Since metals are usually positively charged in solution and may tend to avoid being incorporated into an anodic film, a conversion of the metals to neutral or anionic species appeared desirable where possible. Cadmium solutions were complexed with cyanide and lead with EDTA. Soluble plumbous hydroxide (usually referred to as plumbite) was prepared by dissolution of a lead salt in strong base.

McNeill (Ref. 3) anodized Cd metal in a niobate bath at high, spark-producing currents by employing potentials above the breakdown voltage of the initially formed anodic film. The insoluble material that had fallen off of the anode was characterized as Cd_2NbO_7 after firing. Gruss and McNeill (Ref. 4) have anodized a variety of metals in aluminate, tungstate and silicate baths at sparking potentials. Alumina or spinels, tungsten oxide and silicates were identified in the anode products along with oxides of the anode metal. The authors attribute the formation of these refractory products to very high, local temperatures caused by the spark-action.

Advantage might be taken of the localized high temperatures produced by anodic spark reactions in forming the proper high temperature phase of the high dielectric mixed metal oxides in film form. Necessary requirements would be the availability of the correct proportions of the metals at the spark site and an adhering and reasonably uniform film product. Several baths were investigated with respect to their ability to form adhering sparked films.

Harwood and Klasens (Ref. 5) have reported that TiO_2 and barium hydroxide

will react to form barium titanate in the liquid range of the hydroxide. Anodized Ti films were reacted with barium hydroxide as a means of preparing the titanate in film form. In an analogous series of experiments, anodized Nb films were reacted with fused KOH in an effort to produce KNbO_3 .

In the preparation and sintering of a film consisting of separate, mixed oxides, a failure to produce a high dielectric might be due to faulty composition or to improper or insufficient heating conditions. In order to separate the variables and investigate only the heating effects, a number of Ti films were provided with electrophoretic coatings of commercial BaTiO_3 powder and fired under various conditions. Some Zr substrates with anodic films were also fired.

Section II

EXPERIMENTAL PROCEDURE AND RESULTS

A. Materials, Equipment and Technique

The anodizing cell design, counter electrodes, and capacity and loss evaluation techniques have been described in the First Quarterly Report (Ref. 2).

During this quarter, all capacity measurements were made with the mercury counter electrode (area of $1/20 \text{ cm}^2$) and all bath volumes were 250 ml unless otherwise specified. After anodization, the films were routinely rinsed with distilled water and dried at 110°C for at least 30 minutes prior to measurement.

References will be made in the text to arcs or scintillations observed during film growth. The former were large individual events giving current surges and leading to the puncture of the film and usually the creation of fused debris outgrowths. The scintillations, on the other hand, were multiple small sparks (usually associated with the growth of thicker, opaque films) observed during steady current conditions.

The metal substrates to be anodized were all cut from 5 mil thick sheets: Ti No. 55A from Titanium Co. of America; Nb No. 89A622-51-23H0114 from Fansteel Metallurgical; and Zr from Carborundum Metals. The potassium silicate solution employed in some baths was Kasil 88 from Philadelphia Quartz Co., containing 9% K_2O and 20% SiO_2 by weight.

High resistance measurements were made on a Lockheed-designed, variable voltage, DC megohmmeter. Breakdown potentials were determined by noting the shape of the hysteresis curve displayed on a Tetronix, Type 575, Transistor-Curve Tracer using half-wave rectified AC. Both types of measurements were made using silver paint counter electrodes. Parallel or series equivalent circuit capacity measurements are denoted by the subscript on the loss value (as D_p or D_s).

B. Films Formed on Nb in KOH-Plumbite Baths

The baths were prepared by adding lead acetate trihydrate to a solution of potassium hydroxide. The resultant solutions contained excess potassium hydroxide, potassium acetate, and a soluble lead hydroxide (the latter usually referred to as plumbite).

Using a bath prepared from 20g KOH and 5g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, untreated Ti strips, the current limited up to 40 mA/cm^2 , and limiting potentials of 15 to 20 volts, a two stage film growth was observed. A thin, transparent, blue film formed rapidly and the current dropped to a variable

fraction of the preset limit. Black dots then appeared, scattered over the film surface. On prolonged anodization (several hours) the black dots coalesced giving the appearance of a thick, dendritic, black film covering a major portion of the initially formed thin, blue film. Capacity and loss values ranging from 2 microfarads at $D_s = 0.25$ to 7 microfarads at $D_s = 1.0$ were obtained for strips having an anodized area of 2.5 cm^2 per side. For any given strip the measured capacities were relatively insensitive to the area of the mercury or silver paint counter electrodes employed.

Thick, black film were grown by anodizing for one hour (under the conditions described above) and then the films were stripped off of the Ti substrates by reanodizing in a 25 volume percent $\text{Et H}_2\text{PO}_4$ bath. A spectrographic analysis yielded a niobium content of 0.15 weight percent in the stripped film.

Various Nb substrate pre-treatments and anodization parameters were investigated to improve the quality of the KOH-plumbite bath films and to prepare them faster. Soaking the strips in H_2SO_4 -chromate (glass cleaning solution) prior to anodization, and then anodizing without current limitation gave the fastest growing and most uniform black films. Under these conditions, an initial current surge of about 200 ma/cm^2 was observed. A silver paint counter electrode drying time of about 40 hours at 110°C appeared to give minimum losses. (Preheating the Nb strips at 400°C , precoating them with an electrolytic lead film, pre-anodizing in a plain KOH bath, and reducing the electrode spacing of the anodization cell did not appear to be of any benefit.) The optimum forming potential was 15 to 20 volts. Raising the voltage much above 20 led to scintillations and apparently a different type of film growth mechanism. In those cases, the usual black film were not obtained and the capacities were reduced drastically.

Examples of capacity and loss data for strips exhibiting uniform black films are listed in Table No. 1. The capacities were still roughly proportional to the film area (two sides - 5 cm^2) and independent of the area of the counter electrode. Several of the films were given further electrical tests. Strip 104C exhibited a resistance of 12 megohms at 1.5V DC and one megohm at 2.0V DC. For strip 1C the DC resistance was 20 megohms at 2V and one megohm at 8V. Typical curve tracer observations are given in Table No. 2. The testing potentials were raised rapidly taking only a few minutes to reach the breakdown point. The DC resistance and breakdown potentials were measured using silver paint counter electrodes with the counter electrodes always at negative (or ground) potential. Reversing the current flow resulted in breakdown at only a few volts.

TABLE No. 1

Capacity and Loss Values for Thick Black Films Formed on H_2SO_4 -Chromate Soaked Pb Strips in KOH-Plumbite Baths at 20 Volts. Current Unlimited. Silver Paint Counter Electrode Drying Time Approximately 20 Hours.

Strip No.	Bath Concentration	Forming Time (min)	Capacity per Strip (nF)	Loss (D_s)
	$\frac{g\ KOH}{g\ Pb(C_2H_3O_2)_2 \cdot 3H_2O}$			
104C*	12/4	60	360	0.15
107A	15/4	60	1100	0.35
1B	20/4	30	660	0.13
1C	20/4	30	650	0.15
2C	12/4	22	630	0.10
4A	20/4	90	370	0.30
4B	20/4	120	440	0.40
1DA**	3/1	15	1100**	0.30

* Pb strip soaked in 8N HNO_3 .

** Mercury counter electrode used.

TABLE No. 2

Strip No.	Current at 20V (ma)	Breakdown Potential (volts)
104C	2.0	27
107A	3.5	28
1B	3.5	25

C. Films Formed on Ti in KOH-Plumbite Baths

The baths were prepared as discussed in Section II B. (The symbol 3/1, for instance, will refer to 3g KOH and 1g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ used in the preparation of the bath.)

The thick black films grew in the same manner as did those on Nb substrates. Films formed in a 3/1 bath under various conditions are listed in Table No. 3. When the bath concentration was increased to 20/5, more variable films were produced with capacities ranging from 500 to 35,000 nF per strip at loss values of about two -- this with forming currents limited at 10 or 35 ma/cm². When the forming current was not limited, the thick films were loose and powdery. Here, as in the case of the thick black films on Nb substrates, the capacities were roughly proportional to the total anodized area of the strips.

By employing short anodizing times, more dilute baths, or higher forming potentials, films could be produced on Ti, in KOH-plumbite baths, that were thin and multicolored and did not exhibit a total anodized area-capacity dependence. They were usually produced with a thin deposit of gold or brown colored dust on the surface. Up to about 40 volts these films exhibited high losses (D values from one to two) and capacities ranging from 400 to 10,000 nF/cm². At higher forming potentials, films with losses less than one were obtained. Table No. 4 lists only those films having capacities of 200 nF/cm² or higher and losses of one or lower. Measurements made using aqueous LiCl counter electrodes (after measuring a given strip using mercury) yielded higher capacities and the same or slightly lower losses. Firing at 800°C in air drastically reduced the capacity values of these anodized films.

D. Films Formed on Ti in Other Lead-Containing Baths

The results with simple lead acetate baths and with the lead complexed by EDTA are presented in Table No. 5. The Bath Concentration numerator refers to the grams of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ and the denominator to the grams of $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$.

Other baths were prepared by dissolving $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in 100 ml of Kasil 88 and diluting to 250 ml. Using 0.1 g lead acetate, a forming potential of 125 volts, and current densities of 10 to 150 ma/cm², films with capacities of about 40 nF/cm² at $D_p = 0.15$ were produced. Scintillations were observed at the highest current densities and the film values were not internally consistent. When the lead acetate content was increased to 1.0 g, the forming potential could not be raised past about 70 volts at current densities to 30 ma/cm².

One Ti strip was anodized in a bath prepared from 5g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ and 5 g $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. After 6 minutes at high current, a potential of only 25 volts was attained and arcing set in. The resulting film had no measurable capacity.

Table No. 3

Capacity and Loss Values for Thick Black Films
Formed on Ti Strips in a 3/1 KOH-Plumbite Bath
at 20 Volts. Current Limited to 35 ma/cm.

Strip No.	Strip Pretreatment	Forming Time (min)	Final Current (ma/cm ²)	Capacity per Strip (nF)	Loss (Dp)
13E	Acetone	2	10	1500	0.61
13B	HF-HNO ₃	15	11	1000	1.0
13A	H ₂ SO ₄ -Chromate	15	8	850	0.47
13D	Acetone	25	6	940	0.30

Table No. 4

Capacity and Loss Values for Thin Films Formed
on Ti Strips in KOH-Plumbite Baths

Strip No.	Pretreatment	Forming Voltage	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Conc.	Capacity (nF/cm ²)	Loss (Dp)
Forming Voltage Reached Limit								
13G	Acetone	50	1	35	10	3/1	400 ^{a,b}	0.19
64A	Acetone	120	30	35	30	2/0.1	280	0.50
Forming Voltage Did Not Reach Limit								
18A	Acetone	40	20	35	35	12/4	1400	0.79
56D	Acetone	45	5	10	10	1/0.05	800	1.0
61B	Acetone	45	30	10	10	0.3/0.1	640	0.75
56E	Acetone	50	3	10	10	1/0.05	600 ^b	0.55
56G	Acetone	55	2	10	10	1/0.05	200	0.30
61A	25% HF	55	30	10	10	0.3/0.1	280	0.45
13I	Acetone	70	2	35	35	3/1	200 ^b	0.30

a - A series equivalent circuit measurement

b - Brown dust wiped off surface prior to measurement

Table No. 5

Tl Anodized in Lead Acetate Baths
With and Without EDTA Added

Strip No.	Voltage Limit	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Conc.	Capacity (nF/cm ²)	Loss (D _g)
68B	150	15	6	2	1/0	160*	0.24
68A	150	3	25	4	1/0	140*	0.22
36B	100	22	160	3	5/0	60	0.26
72A	150	10	10	4	1/0.3	120	0.055
72B	150	15	35	15	1/0.3	150	0.090
72C	100	30	10	2	1/0.3	180	0.090
72D	50	40	10	10	1/0.3	300	0.13

* Parallel equivalent circuit measurements

E. Films Formed on Zr in Lead-Containing Baths

Films were grown in a simple bath made from 5 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$. The capacity and loss values are given in Table No. 6. The films were an opaque gray when formed at 100 volts or greater.

Efforts to grow the high capacity per strip, thick, black films (as are obtained on Nb and Zr substrates in a KOH-plumbite bath at 20 volts) were not successful. A uniform black film was obtained on Zr in a KOH-plumbite bath at 50 volts but it had no measurable capacity. Scintillations were observed in a 9/3 KOH-plumbite bath at 70 volts and arcing at 130 volts. Increasing the KOH concentration decreased the voltage at which the scintillations first appeared. Capacities of the spark-grown films were low -- the highest observed value was 0.6 MF/cm^2 .

A thick, white film was grown on Zr at 300 volts in a bath containing 5 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ and 5 g $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. After 13 minutes the current was still passing at the rate of 120 ma/cm^2 . The capacity of this film was 0.2 nF/cm^2 .

F. Films Formed on Nb, Ti and Zr in Simple KOH Baths

Nb strips anodized at 20 volts in 12g KOH and 2g KOH bath concentrations yielded only thin blue films. The current dropped rapidly from the initial 35 ma/cm^2 limit to 0.2 ma/cm^2 and a maximum of 65 volts was reached. A three minute anodization at this level produced a film with an average capacity of 120 nF/cm^2 at $D_s = 0.022$.

The results with Ti strips are presented in Table No. 7. Pretreatment in all cases was an acetone wipe. No black films were observed.

One Zr strip was anodized in a 50 g KOH bath to determine whether a thick, spark-type film could be grown. Sparks were observed at 80 volts and 140 ma/cm^2 . After 10 minutes the strip still had a thin, colored film with breakdown spots. The capacity was variable and low.

G. Films Formed on Ti in Barium-Containing Baths

The simple EtH_2PO_4 and the EtH_2PO_4 -barium phosphate baths have been described previously². Films produced in these baths under high, limited current anodizing conditions are listed in Table No. 8. In the simple bath, arcing was observed only in the gas phase (produced by a gas bubble collected under the jig). In the barium-containing bath, arcing took place randomly over the strip surface producing small areas of white debris. Forming times were made short to preserve enough unsparked area to allow placement of the counter electrode. The films were measured after drying at 110°C and then after firing at 800°C in air. The white, arc product areas had much lower capacities than the unsparked gray film areas listed in the table.

Titanium strips were also anodized in solutions containing 3g $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ or 5g $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot n\text{H}_2\text{O}$. Capacity and loss values after drying at 110°C and after firing at 800°C are listed in Table No. 9. Arcing took place at 195 volts in the hydroxide bath. The acetate bath-formed films, after firing

Table No. 6

Capacity and Loss Values for Films Formed
on HF-HNO₃-Etched Zr Strips in a Lead Acetate Bath

Strip No.	Forming Voltage	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Capacity (μF/cm ²)	Loss (D _s)
39B	100	60	40	1	120	0.49
42C	100	2	120	6	48	0.14
36A	100	12	40	7	40	0.08
36E	100	1	40	3	20	0.006
42A	20	30	60	1	40	0.032
39A	150	12	45	3	20*	0.16
42E	200	1	80	80	20	0.16
42G	250	30	80	3	10	0.07
42F	300	3	140	100	8	0.07

* A parallel equivalent circuit measurement

Table No. 7

Capacity and Loss Values for Ti Strips Anodized
in Simple KOH Baths

Strip No.	Forming Voltage	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Conc. (g KOH)	Capacity (nF/cm ²)	Loss (Dp)
67B	35 ^a	30	5	5	1	30 to 130	0.40
19A	50	30	20	4	3	280	0.24
23A	50	140	20	2	1	110 ^b	0.21
67A	120	15	35	35	1	20 to 140	0.40

a - Forming voltage did not reach limit

b - Series equivalent circuit measurement

Table No. 8

Capacity and Loss Values for Ti Strips Anodized at High Currents
in Simple EtH_2PO_4 and EtH_2PO_4 -Barium Phosphate Baths

Strip No.	Bath	Forming Time (min)	Max. Voltage Attained	Current Density (ma/cm^2)	After Drying Capacity (nF/cm^2)	After Drying Loss (D_g)	After Firing Capacity (nF/cm^2)	After Firing Loss (D_g)
42M	Simple	2	—	190	13	0.55	130	0.27
42N	Simple	1 $\frac{1}{2}$ *	380	190	7.2	0.42	8.6	0.67
45R	with Ba	$\frac{1}{2}$	130	210	70	0.75	20	1.3
45S	with Ba	$\frac{1}{4}$	130	240	180	0.53	80	0.7

* Bath boils after 1 $\frac{1}{2}$ minutes

Parallel equivalent circuit measurement

at 800°C, exhibited lower capacities and higher losses than before firing. The values changed too fast during measurement to obtain significant readings.

Ti strips were also anodized in a bath of fused $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ contained in a nickel crucible serving as the anode. The barium hydroxide was maintained somewhat above its melting point of 78°C. No stop-off was used. A constant, limited current was employed. At 60 ma/cm² a voltage of 30 was reached. The film had a capacity of 0.6 nF/cm² at $D_s = 0.03$. At 160 ma/cm² a voltage of 50 was reached with arcing. The capacity of the resulting film was about 0.08 nF/cm² on all areas.

H. Films Formed on Ti in a Pyridine-Water Bath

The starting bath was a suspension of BaTiO_3 particles in pyridine. The cell was similar to that used in the other anodizations except that the cathode was reduced to fit in a 100 ml beaker. The use of the stop-off jig was not necessary. The anodization voltage in each case was 400 volts. The current densities were low only reaching 3 ma/cm² after a large amount of water was added to the bath. Since no evidence for the incorporation of particles into the films was found, the films can be considered as single phase. The first film formed was the thin, transparent type. As the water content was increased an increasing fraction of the strip was covered by a thick, white deposit in the form of small dots. Capacity and loss values are given in Table No. 10.

I. Films Formed on Nb in an Ethyl Acid Phosphate Bath

The bath contained 50 ml EtH_2PO_4 and 200 ml H_2O . Anodizations were carried out for 15 to 30 minutes, at which time, the current dropped off quickly (strips 68B and 73C are exceptions). The films were dried at 110 to 200°C. The results are listed in Table No. 11.

J. Films Formed on Nb in Cadmium-Containing Baths

The simple baths were prepared by dissolving 5 or 20g of Cd SO_4 . Alternately, one g KOH or 6.5g KCN were also added.

The results are listed in Table No. 12. When silver paint counter electrodes were employed, the capacities were lower and the losses higher. The simple baths produced thin, transparent, rose-colored films at 100 volts. At 200V the film was gray. Scintillations were observed when anodizing to 300 volts in the KOH-containing bath. The film on strip 26B was a thick, ceramic white. The cyanide containing bath produced gray films with scintillations at the higher current densities.

K. Films Formed on Nb, Ti, and Zr in Miscellaneous Baths

One strip of each substrate metal was anodized in a bath of 250 ml of Kasil 88. With Nb, scintillation set in at about 150 volts and arcing at about

Table No. 9

Capacity and Loss Values for Ti Anodized in
Barium Hydroxide and Barium Acetate Baths

Strip No.	Voltage Limit	Forming Time (min)	Current Limit (ma/cm ²)	Final Current (ma/cm ²)	Bath	After Drying Capacity (nF/cm ²)	After Drying Loss (D _g)	After Firing Capacity (nF/cm ²)	After Firing Loss (D _g)
21A	50	30	20	9	Hydroxide	300	0.5	240	0.4
21B	100	30	160	30	Hydroxide	320*	0.4	28	0.08
21C	150	30	160	160	Hydroxide	Variable	Variable	30**	0.7
21D	195	185	160	4	Hydroxide	0.2	Low	---	---
32A	100	35	40	2	Acetate	2.0	0.25	---	---
32B	280	45	160	10	Acetate	38	0.09	---	---

* Parallel equivalent circuit measurement

** Value listed is for arc debris areas. Non sparked areas had low C and high D

Table No. 10

Ti Anodized in Pyridine-Water Baths at 400 Volts

Strip No.	Water Added	Forming Time (min)	Capacity (nF/cm ²)	Loss (D)
55A	None	15	200	0.27
55B	Slight	5	6	0.17
55C	Large	15	0.6	0.10

Table No. 11

Nb Strips Anodized in an Ethyl Acid Phosphate Bath

Strip No.	Forming Voltage	Current Density (ma/cm ²)	Capacity (nF/cm ²)	Loss (D)	Remarks
68B	150	20	60	0.004	(1)
68C	195	25	1.0	0.01	(2)
68D	195	30	1.0	0.003	(2)
73B	202	35	1.4	0.007	(2)
73C	235	55	2.0	0.013	(3)

(1) Current drops very quickly. Thin, transparent film.

(2) Opaque, rose-gray film. Incomplete coverage.

(3) Current drops only by $\frac{1}{2}$ after 30 minutes. Gray, opaque film. Excellent coverage.

Table No. 12

Capacity and Loss Values for Films Formed on
Nb Strips in Simple Cadmium Sulfate Baths

Strip No.	Forming Voltage	Forming Time (min)	Idmiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Conc.	Capacity (nF/cm ²)	Loss (D _g)
34C	50	2	160	0.2	20/0	180	0.038
34B	100	30	160	2	20/0	100	0.022
34A	100	30	160	0.1	20/0	110	0.04
30A	100	30	20	0.1	5/0	120	0.012
26A*	190	10	160	1	5/0	70	0.006
30B	200	30	160	1	5/0	50	0.008
With 1g KOH added to bath							
26C	100	30	160	0.2	5/1	120	0.011
26B*	300	short	160	120	5/1	0.6 to 8.0	0.1 to 0.6
With 6.5g KCN added to bath							
24A	195	---	35	3	5/6.5	10	0.025
24B	200	---	160	60	5/6.5	8	0.03
24C	200	---	160	80	5/6.5	12	0.5

* Nb Strip was preplated with a film of Cd metal

220 volts at high current density (of the order of 100 ma/cm^2). After 12 minutes near 220 volts a film with a capacity of 0.1 nF/cm^2 at $D_p = 1.5$ was produced. With Ti, scintillation began at about 100 volts. After 30 minutes at 185 volts the current dropped from 160 to 1 ma/cm^2 and a film with a capacity of 0.08 nF/cm^2 at $D_p = 1.0$ was produced. A Zr strip held for 93 minutes at 100 volts dropped from 20 to 0.1 ma/cm^2 . The resulting film had a capacity of approximately 4 nF/cm^2 at $D_p = 0.35$.

Niobium strips were anodized in a very dilute solution of NaHCO_3 . At 195 volts, variable-valued films were produced. One strip held 30 minutes at 150 volts (initial current density was 20 ma/cm^2) produced a film having a capacity of 80 nF/cm^2 at $D_s = 0.02$.

Titanium strips were anodized in a bath of ammonium citrate prepared by dissolving $5.3\text{g } \text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ in water and adding NH_4OH to a pH of 5 to 6. Only thin, interference color films could be grown using forming potentials to 195 volts and current densities to 55 ma/cm^2 .

Zirconium strips (etched in HF-HNO_3) were anodized at 100 volts in a bath prepared by dissolving $5\text{g } \text{ZrO}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ in water. In about 30 minutes the initial, high current densities dropped to 0.2 ma/cm^2 . The capacities of the resulting films averaged 0.8 nF/cm^2 at D_s from 0.03 to 0.07. Heating one of these films to bright red in a bunsen flame resulted in a ten fold increase in loss.

L. Reaction of Anodized Nb Films with Potassium Hydroxide

Niobium strips containing opaque films grown in the EtH_2PO_4 bath were dipped briefly into fused KOH. (Too long an immersion time resulted in complete dissolution of the film and attack on the metal substrate). After rinsing off the excess KOH with water, a change in film color from gray or rose-gray to white was observed. After drying at 110°C capacities of approximately $60 \text{ microfarads/cm}^2$ at $D_p = 4$ were observed. After a few minutes out of the oven the capacity fell off and the loss increased. After reheating to 400°C , the capacity was partially restored to about $4 \text{ microfarads/cm}^2$ but the loss was 33. Reanodizing the dipped films in the EtH_2PO_4 resulted in values not as good as ordinary anodized films.

Niobium strips with the gray films grown in the cadmium containing baths were also dipped in fused KOH to produce a white product. Using the No. 24 strip series (see Section J.) reacted films with an average capacity of 0.8 nF/cm^2 at $D_s = 0.01$ to 0.06 were produced after rinsing and drying. Dipped strip no. 26B was 18 nF/cm^2 at $D_s = 1.0$ after a similar treatment.

M. Reaction of Anodized Ti Films with Barium Hydroxide

Opaque, gray films were formed on Ti strips by anodizing in an EtH_2PO_4 at 20 ma/cm^2 to 225 volts. After drying, parts of the strips were dipped for a few seconds into fused $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (melting point about 78°C) to form a thick coating. The coated strips were heated in air briefly to 550°C and then held for 30 minutes at 400°C . The resultant thick, flaky coating was washed off with water, the strips dried at 110°C , and the capacity

measured with a mercury counterelectrode. The dipped portions of the film exhibited a capacity of from 0.4 to 0.8 nF/cm² while the undipped portions were higher at 4 to 10 nF/cm². The loss values were low — less than one percent. Treating the reacted strips with the strongly acid EtH₂PO₄ anodizing bath (to remove traces of barium hydroxide) and then rinsing and drying raised the capacities of both sections but also increased the loss:

Undipped - 15 nF/cm² at D = 0.25
Dipped - 1.3 nF/cm² at D = 0.1.

Refiring at 850°C for one hour in air raised the values for the dipped film area to 3 nF/cm² at D = 0.2 and simultaneously reduced the capacity of the undipped film area.

Thicker, more porous anodic films were formed on Ti strips by anodizing in the EtH₂PO₄ bath for 1½ minutes at 140 ma/cm² to approximately 300 volts. These films were allowed to stand in the fused Ba(OH)₂·8H₂O for about one minute. The strips with their thick dip-coats were then fired in air for 3½ hours at 400°C followed by ½ hour at 850°C. After removing the unreacted excess by dissolving in EtH₂PO₄ and rinsing and drying, the portions of the films exposed to barium hydroxide contained three distinct types of regions: relatively smooth black film with an average capacity of 1.2 nF/cm² at D = 0.25; cracked and peeling white product area with an average capacity of 0.40 nF/cm² at D = 0.5; and a very thin, yellow film area (where the thick films had fallen off) exhibiting a widely variable high capacity averaging about 6000 nF/cm² at Dp = 2.5. The film areas not exposed to barium hydroxide gave an average capacity of 1.0 nF at D = 0.1.

In an alternate procedure the anodized Ti strips were dipped into fused Ba(OH)₂ which has a melting point of about 408°C. In this case the reaction proceeded directly to give a rough and porous white product which did not adhere to the Ti substrate. Capacity measurements could not be made.

N. Heat Treatments of BaTiO₃ Deposits on Ti Strips

Approximately one gram of BaTiO₃ powder was ground briefly with a small amount of pyridine in a mortar. The slurry was added to a 100 ml size cell and diluted to 75 ml with pyridine. Deposition was carried out with the axial Ti strip at 195 volts negative. Excellent coverage of BaTiO₃ was obtained in ½ to one minute.

Capacity and loss values following various heat treatments are presented in Table No. 13. No sintering was observed for the BaTiO₃ deposits heated to 1000°C in air or to 1080°C in vacuum. The deposits still adhered to the Ti substrate, but could be easily wiped off with a towel. After firing at 1250°C in vacuum the BaTiO₃ deposit had a sintered, metallic gray appearance. Deposits fired at both temperatures in vacuum were highly conducting whereas the air fired deposits were highly resistive. The vacuum-heated deposits could be made resistive by heating in air. (See Table No. 14).

O. Heat Treatments of Anodized Zr Strips

Zirconium strips having gray films formed in a lead acetate bath were heated at 1150°C for 15 minutes in vacuum. The films disappeared leaving a bright,

Table No. 13

Film Type	Heat Treatment	Capacity (nF/cm ²)	Loss (D)
Bare Ti	800°C, Air, 1 hr.	28	0.14
Thick BaTiO ₃ Deposit on Ti	Dried at Room Temp. 800°C, Air, 1 hr. 1000°C, Air, $\frac{1}{2}$ hr. 1080°C, Vac., 1/3 hr. 1250°C, Vac., $\frac{1}{2}$ hr.	0.3 1.0 0.6 100 x 10 ³ 60 x 10 ³	0.15 0.5 0.3 40 33
Film Grown	800°C, Air, 1 hr.	40	0.3
Under BaTiO ₃	1000°C, Air, $\frac{1}{2}$ hr.*	3.0	0.2
Ti Strip Containing BaTiO ₃ Deposit Anodized in EtH ₂ PO ₄ Bath	1000°C, Air, $\frac{1}{2}$ hr.	3.0 to 24	0.2
Film Grown Under Combined Deposit and Anodization	1000°C, Air, $\frac{1}{2}$ hr.	26 x 10 ³	30

* A thick white film.

Table No. 11

Original Vacuum Heat Temperature	After Heating to Red Heat in a Flame		After Firing $\frac{1}{2}$ hr. at 800°C in Air	
	Capacity (nF/cm ²)	Loss (D)	Capacity (nF/cm ²)	Loss (D)
1180°C	100	0.07	26×10^{-3}	0.15
1250°C	400	0.6	2.4	0.16

coarse-grained metallic surface. A zirconium strip having a very thick white film formed in a zirconyl nitrate-lead acetate bath was heated at 1250°C for 30 minutes. A gray, low resistance film remained; however, the substrate metal was brittle and shattered into small fragments.

Section III

DISCUSSION

The thick, black films grown on Nb to 20 volts in KOH-plumbite baths (Section B) may be considered to consist of two layers: a capacitive, high resistance, inner layer and a conducting, non-capacitive, outer layer. The outer layer, acting as a mildly resistive, "built-in" counter electrode causes the capacity measurements to be independent of the area of the metallic contact employed. It also causes the loss to be higher than expected (from capacity and resistance measurements) by contributing a series or contact resistance.

If one assumes the effective area of the capacity measurements on the thick, black films to be the total anodized area of both sides of the strips, then the unit area capacity of these films is on the order of 0.1 F/cm^2 . This is not a high value for a 20 volt film if the effective capacitive layer is very thin. Higher microfarad-volt products were obtained by anodizing Nb in simple basic baths. Although a small Nb content was found in the stripped, black films, the postulation of the formation of a double oxide type high dielectric is not required. The bulk of the black film is probably a conducting form of lead oxide.

One of the interesting properties of the thick, black films on Nb is their ability to withstand higher voltages than the forming voltage before breakdown.

Titanium anodized at 20 volts in a KOH-plumbite bath (Section C) apparently gives the same type of double layer black films as are obtained with Nb. For films with losses less than one, the capacity of the Ti-based films averages about 0.2 F/cm^2 (Table No. 3) or roughly twice that of the Nb-based films. The losses were also generally higher, and the black films could not be made as uniform.

Anodized Ti films, prepared in KOH-plumbite baths, without conducting black layers, exhibited capacity - voltage products ranging from 13 to 56 F-V/cm^2 for films with losses less than one (Table No. 4). These products are larger than one might expect for ordinary, non-rutile films (with dielectric constants around 30) and could indicate the presence of some higher dielectric material. However, the loss values of these films were relatively high and so were the final anodization currents — both criteria indicative of the formation of thin or porous films. A porous film or one thinner than normal for its forming potential would also give a high capacity - voltage product. Titanium anodized in simple KOH baths (Section F, Table No. 7) also gave relatively high loss films; however, the capacity-voltage products were lower than those obtained in the KOH-plumbite baths. Thus, the presence of high dielectric material in the KOH-plumbite bath films cannot be ruled out.

The reason for considering films exhibiting only a small improvement in capacity value, over that to be expected for a single oxide film, is due to the behavior of capacitances in series. The presence of even a thin layer of low dielectric material in a high dielectric film would drastically reduce the measured capacity of that film.

Among the films formed on Ti in lead containing baths, those produced in the lead acetate - EDTA bath (Section D, Table No. 5) gave the lowest loss values. Films formed at 100 to 150 volts exhibited 18 to 22 F-V/cm² products at losses less than 0.1. Neglecting porosity effects, the capacity-voltage product is over twice the value one would expect for ordinary anodized Ti films.

The thick, black films giving high capacities per strip were not successfully formed on Zr substrates (Section E). Zirconium anodized in a simple lead acetate bath produced some of the lowest loss films of any formed in lead containing baths (Table No. 6). The corresponding capacities were too low to be significant. Relationship between the capacity and loss is illustrated by the series of values obtained at a 100 volt forming potential in this system.

Niobium anodized in simple CdSO₄ baths (Section J, Table No. 12) at 50 to 200 volts produced films with 9 to 13 F-V/cm² products and some fairly low loss levels. Comparable thin films on Nb from non-cadmium containing baths gave the following capacity-voltage products: 8 F-V/cm² from KOH (Section F); 9 F-V/cm² from EtH₂PO₄ (Table No. 11, Strip 68B only); and 12 F-V/cm² from NaHCO₃ (Section K). No substantial difference in dielectric quality is therefore indicated between CdSO₄ bath-produced films and the others. When the cadmium in the bath was complexed with cyanide to provide anions, the resulting films had lower capacities than those produced from the uncomplexed baths.

Niobium anodized in an ethyl acid phosphate bath (Section I) produced two kinds of films. Below about 185 volts a rapidly-forming, thin, translucent film was grown. At higher potentials an apparently thicker, opaque film was produced. The opaque films had reduced capacity values but exhibited ability to be formed to low loss levels.

The anodization of Ti in pyridine was not pursued because of the lack of evidence for the formation of a mixed metal oxide (Section H). However, the use of a pyridine bath containing little or no water appears promising with respect to the formation of higher than usual capacity-voltage product, single phase films if the loss value can be reduced to an acceptable level.

The high current density formed films on Ti in the ethyl acid phosphate-barium phosphate bath were generally unacceptable because of the damage produced by the arcing (Section G, Table No. 8). The non-arc'd areas were of variable capacity and high loss and became worse on firing. Among the Ti strips anodized in a simple, aqueous barium hydroxide bath (Table No. 9) number 21B exhibited an interestingly high capacity, but failed to maintain that value on firing. Titanium anodized in aqueous barium acetate or fused Ba(OH)₂·8H₂O gave only relatively low capacity films, and, in the latter, only low forming potentials could be achieved.

Several bath and substrate combinations appear promising with respect to the formation of adherent, reasonably uniform films under high potential, high current, spark producing conditions. Niobium in a CdSO₄-KOH bath (Section J) and zirconium in a Pb(C₂H₃O₂)₂ - ZrO(NO₃)₂ (Section E) bath produced the required films at 300 volts. Other combinations which showed promise but were not tried at so high a forming potential were: Nb in a cyanide complexed cadmium bath (Section J); Zr in a zirconyl ni-

trate bath and Nb, Ti and Zr in a Kasil 88 bath (Section K). The addition of lead acetate to the Kasil 88 bath reduced the forming potential which could be achieved with Ti (Section D). The capacities of the high current density, spark-produced films were all low -- a not unexpected result for very thick films unless the exact requirements for the formation of a high dielectric, mixed metal oxide had been fortuitously met.

The anodized Nb films dipped in fused KOH (Section L) apparently reacted sufficiently to alter their chemical composition; however, the resulting low capacities indicate that the reacted films contained insufficient amounts or the wrong form of the desired high dielectric KNbO_3 . Anodized Ti films contacted with molten barium hydroxide (Section M) also reacted to produce a different type of film -- presumably containing BaTiO_3 . The product was invariably flaky and non-adherent. In those cases where enough product remained on the strip to be measured, the capacities were low.

The results of firing the coarse-grained electrophoretic deposits of BaTiO_3 on Ti substrates (Section N) show that no appreciable sintering takes place much below 1250°C . Due to the growth of low capacity films on the substrate, air firing appears unadvisable in the absence of a highly protective coating. The anodized film afforded such protection in air to 1000°C because the reaction with the substrate led to a high capacity, conducting, thin film. (A film of this type underlying a desirable high dielectric, high resistance layer would not reduce the capacity of the composite device). Firing in vacuum produced a conducting form of BaTiO_3 , presumably through the loss of oxygen. The high capacity could not be maintained (even with the sintered deposit) on refiring in air.

Relatively thin oxide films on Zr substrates disappear when heated at 1150°C in vacuum (Section O). The same effect was observed when anodized Ti was heated to 1100°C in argon² and may be attributed to the solution of the film oxygen in the metal substrate. When a very thick, anodized film on Zr was heated at 1250°C in vacuum, some film remained on the surface, but the metal substrate was destructively embrittled.

SECTION IV

PLANS FOR FUTURE WORK

The possibility of incorporating high dielectric material in thin films formed in soluble metal containing baths should be pursued. A primary goal would be the production of reasonably low loss films.

Since the initial investigations have shown that adherent films can be formed under sparking condition, variations in bath contents should be explored. A propitious bath might be one that contained both of the desired film metals in soluble form. Local heating caused by the spark might then cause a mixed metal oxide of the desired high dielectric form to be deposited.

Anodization of Ti in a fused salt bath containing barium hydroxide at about 400°C might lead directly to the formation of a barium titanate film.

Since the anodized Nb films reacted with KOH have been adherent, reaction techniques other than dipping in fused KOH might be explored. Saturation of the film with a stoichiometric quantity of aqueous potassium compound followed by firing at an intermediate temperature might be a useful approach.

SECTION V

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